THE EFFECT OF FILM COMPOSITION ON THE TEXTURE AND GRAIN SIZE OF $CuInS_2$ PREPARED BY SPRAY PYROLYSIS

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$CuInS_2$ was deposited by spray pyrolysis using single-source precursors synthesized in-house. Films with either (112) or (204/220) preferred orientation always showed Cu-rich and In-rich composition respectively. The In-rich (204/220)-oriented films always contained a secondary phase evaluated as an In-rich compound, and the hindrance of (112)-oriented grain growth was confirmed by glancing angle X-ray diffraction. In conclusion, only the Cu-rich (112)-oriented films with dense columnar grains can be prepared without the secondary In-rich compound. The effect of extra Cu on the grain size and the solar cell results will be also presented.

REVIEW ABSTRACT

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The main objective of this work is the development of thin film space solar cell materials that can be deposited on large-area flexible lightweight substrates, which will make new designs possible for future space applications by enhancing the mass-specific power - The goal is 1 kw/kg. We previously developed new ternary single-source precursors (SSPs) for chalcopyrite materials and demonstrated $CuInS_2$ thin film deposition using spray pyrolysis processes [1,2].

It is well understood that precise control of composition during film growth is critical for chalcopyrite materials, and the material choice is typically Cu-rich for $CuInS_2$. In comparison, overall Cu-poor films of $Cu(In,Ga)Se_2$ (CIGS) have shown the best performance for thin film solar cells [3]. In principle, Cu-poor composition is desirable for both $CuInS_2$ and CIGS solar cells because the recombination at the interface formed with CdS (the typical buffer layer on top) can be minimized [3]. It should also be emphasized that there should be a Cu-rich stage during the film growth for both $CuInS_2$ and CIGS (even though it is Cu-poor overall) to obtain grain size large enough for making solar cells [4], and the Cu-poor film growth stage is desirable only for the interface removing Cu-S (or Se) phase segregated on top during the Cu-rich stage. There has been a lack of effort to control the film composition systematically to realize the process that includes a Cu-rich region followed by a Cu-poor film growth solely for $CuInS_2$. Only one approach using a bilayer $CuInS_2$ structure without further development has been reported [5].

As the first step towards this, we investigated the composition of $CuInS_2$ films deposited using SSPs, and its effect on texture and grain size. Films were deposited by three spray pyrolysis apparatuses with different configurations. They include a horizontal

atmospheric hot-wall reactor with a plate-type ultrasonic nebulizer (Sonaer Ultrasonics, 2.5 MHz), a vertical atmospheric cold-wall reactor with a commercial ultrasonic nozzle (Sono-Tek, 120 kHz), and a horizontal low-pressure hot-wall reactor with a pulsed aerosol injection system using a commercial automotive fuel-injector (Ford 2M2EA7B). Precursors used in this study include $(PPh_3)_2CuIn(SEt)_4$ and $\{P(n\text{-}Bu)_3\}_2CuIn(SEt)_4$ dissolved in toluene, and Ar was used as the carrier gas. The overall process temperature is typically maintained under 400 °C, and either glass (Corning 2947 or 7059) or molybdenum (commercial foil or deposited) was used as a substrate.

Films with either (112) or (204/220) preferred orientation always showed Cu-rich and In-rich composition respectively regardless of the type of substrate used (fig. 1). Interestingly, the Cu-rich (112)-oriented films with dense columnar grains can only be prepared without the secondary phase. The In-rich (204/220)-oriented films always contained a secondary phase evaluated as an In-rich compound based on the composition analysis using energy dispersive spectroscopy, and further evidenced by results from post-growth annealing and etching experiments and analysis by Raman spectroscopy (fig. 2). The hindrance of (112)-oriented grain growth was also confirmed by glancing angle X-ray diffraction (GAXRD) (fig. 3). It is thought that the observed preferred orientation of the film is related to the molecular structure of the precursors and its subsequent effect on their decomposition kinetics and the nucleation at the surface. The equivalent symmetry between the {102} plane of $CuInS_2$ and the {100} plane of the In compound with a hexagonal structure is also thought to be associated with the observed correlation between (204/220) texture and the In compound. All films deposited in this study showed p-type conduction with an electrical resistivity between 0.1 Ω·cm and 30 Ω·cm. The largest grain size we obtained was about 0.5 μm, and further improvement is expected by implementing an extra Cu-rich growth stage, since we did not observe the existence of the so-called quasi-liquid Cu-S binary phase which is known as a flux layer for large grain growth [4]. The addition of Cu-rich growth stage and the fabrication of solar cells are in progress and will be presented at the conference.

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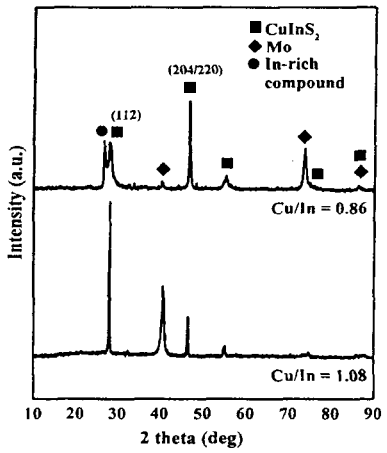

Fig. 1. X-ray diffraction patterns

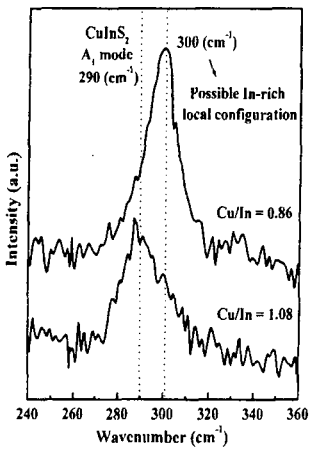

Fig. 2. Raman spectra

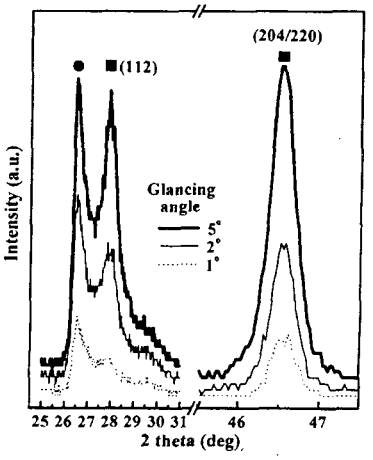

Fig. 3. GAXRD pattern